DEVELOPMENT OF A DETERRED PROPELLANT FOR A LARGE CALIBER WEAPON SYSTEM

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ABSTRACT

There is a continuing need to increase the velocity and associated terminal performance of kinetic energy ammunition as tougher armor targets are encountered. Application of a deterrent, or burning rate reducer, into the surface of standard propellants, together with appropriate changes in geometry and loading density, has been suggested as a means of increasing velocity by as much as ten percent. The attainment of such a desirable performance gain is critically dependent on the deterrent's satisfying certain requirements: (1) chemical compatability with the base propellant, (2) sufficient penetration of the base propellant, (3) diffusion stability of the deterred region over an extended time, (4) ignitability of the deterred layer, (5) sufficient decrease in burning rate. Unfortunately, there exists only a minuscule data base on the way deterrents behave when applied to various base propellants. The deterred propellants used in small arms and anti-aircraft guns were developed by a cut-and-try technique, and the sort of data required for rational design of large caliber weapons systems, e.g. burning rates in the deterred region, is extremely scarce. Since we lack an appropriate data base we have used thermochemical calculations and burning rate estimates to identify promising deterrent/base propellant combinations. The burning rate estimates were based on empirical fits to available closed bomb and strand burner tests with small arms propellants. Several promising deterrent systems are presented, including five candidates which exhibit a decrease in burning rate with no decrease in propellant energy. On the basis of these theoretical predictions, an experimental deterrent coating and analysis study has been initiated at Radford Army Ammunition Plant.

INTRODUCTION

The requirement for increasingly higher muzzle velocities in large caliber weapon systems (LCWS) firing kinetic energy (KE) ammunition has led to theoretical and experimental investigations of high performance propulsion systems employing advanced technologies[1]. The goal of the effort has been to provide a significant increase in the muzzle velocities of existing weapon systems without changing the basic system hardware or operating limits. One highly successful and proven small arms technique for increasing performance under these constraints is that of deterred propellant. The task of applying this small arms deterrent technology to LCWS is complicated by the fact that the bulk of this technology has been empirically derived to meet the requirements of specific small arms applications with little direct emphasis on elucidating the fundamentals of deterrent technology[2]. This Edisonian development approach has been satisfactory in the past for small arms systems due to the relatively small amounts of propellant required and the simplicity of small arms

ballistic testing. It is cost prohibitive in LCWS, where large amounts of propellant are required and the cost of firing even a few rounds can exceed the costs of an entire small arms firing program.

The Ballistic Research Laboratory (BRL), US Army Armament Research and Development Command (ARRADCOM), has initiated a program to elucidate deterrent technology fundamentals so that high performance, deterred propulsion system may be efficiently designed and developed for any large caliber application. This program is currently using the M68, 105-mm tank gun firing KE ammunition as a convenient design base and test vehicle.

BACKGROUND

Producing a higher velocity for an existing projectile requires that more energy be imparted to the projectile during the ballistic cycle. The kinetic energy of a projectile at the end of the ballistic cycle, i.e., at muzzle exit, is proportional to the integral of the projectile base pressure-bore travel curve less resistive forces. One can increase the pressure integral while maintaining the allowable peak pressure by raising the trailing portion of the pressure-travel curve.

Raising the final portion of the pressure curve by increasing the mass rate of gas generation with the fraction of propellant burned is called progressive burning. Two factors that control progressivity are propellant surface area and linear burning rate (or rate of surface regression). These can be tailored to give the desired performance. At any given pressure, the amount of gas generated will be a function of the burning surface area. By selecting a grain geometry that gives an increase in surface as burning progresses, one can increase the mass burning rate and associated pressure after maximum pressure.

The second tailorable factor that controls mass burning rate is the linear burning rate. This is the rate at which the burning propellant surface recedes parallel to itself. In the interior ballistic cycle, the higher the burning rate, the more gas produced per unit time. By tailoring those portions of the propelling charge that burn during the final portions of the pressure curve to burn at a higher rate, more propellant can be consumed in the same time period and more gas will be generated, again, increasing progressivity. One method for providing such a differential burning rate propellant is through the use of deterrents; this has proven highly successful in small arms.

In order to apply this technology in a logical manner to LCWS, we must have a basic understanding of how deterrents work. A deterred propellant is one where the base grain formulation has had a chemical, the deterrent, impregnated into some or all of the exterior surfaces of the propellant granulation. This produces propellant grains with a non-uniform distribution of constituents consisting of a deterred surface layer surrounding or encapsulating the interior, original base grain regions (see Figure 1). The deterrent provides increased progressivity by lowering the base grain formulation's burning rate in the deterred layer. This is illustrated in Figure 2, which shows the closed chamber

burning rate versus pressure behavior for a standard M30, 7 perforation
propellant with ethy centralite (EC). Note that the initial portion of
the propellant has a lower burning rate due to the deterrent. As the
deterred layer is consumed, the burning rate returns to the standard M30
burning rate.

The deterred layer burns during the initial stages of the ballistic
cycle, and it provides a slower rate of gas generation during these
initial stages than would the undeterred base grain. The deterrent
delays the development of the peak chamber pressure in time, and it
allows the projectile to travel slightly farther down the bore. This
increased projectile travel provides a large volume into which the
combustion gases may expand. The result is a peak pressure lower than
that produced by the same charge loading of the undeterred base grain
formulation with identical geometry. This larger volume for pressure
development allows the use of higher propellant loading densities in the
chamber without exceeding the maximum allowable pressure. It also
slightly raises the pressure in the trailing portion of the pressure
curve as seen in Figure 3, thus increasing the integral and imparting
greater energy and velocity to the projectile.

Since the reduced burning rate effect of the deterrent provides the
desired increased progressivity, the obvious question is, how much
improvement in muzzle velocity will deterred propellants privide? An
initial technology demonstration effort by BRL in the 105mm, M68 tank
gun firing KE ammunition and using deterred, 7-perforation M30 propellant
produced a two percent increase in muzzle velocity over the standard
M30 propellant at the same peak pressure[3]. This is not an insignificant
grain as it translates into a 500-meter increase in effective range for
this weapon system. Furthermore, theoretical studies as part of this
initial effort have forecast that increases in velocity of as much as 10 percent
are possible if the deterrent concept is combined with other
proven propellant technologies, such as higher energy propellant formulations
and more progressive grain geometry.[3] The promise of these performance
gains has led to the present theoretical and experimental investigations.
The goal of the present effort is to develop a rational, efficient, and
expeditious method of optimizing the use of deterrent materials in a
given base grain formulation.

CRITERIA FOR DETERRENT DESIGN AND SELECTION

Our first step in developing design criteria was to examine typical
deterrent materials used in small arms development programs. Table I
contains a listing of such materials. An initial analysis revealed that
the one common characteristic of these materials is that they have
negative (or only slightly positive) heats of formation. This is illustrated
in Table II, which lists the theoretical adiabatic isochoric flame
temperature (Tcv) and impetus of these materials at two concentrations
in a homogeneous mixture with M9 propellant. Note that in all cases,
that both the Tcv and impetus of M9 have been reduced.

Table I. Deterrent Candidates

Deterrent	Spherical Formula				ΔH_f Cal/mole	Name/Description
	C	H	O	N		
DNT	7	6	4	2	-14,498	Dinitrotoluene
Camphor	13	16	1		- 78,100	
x-Cellulose	6	10	5		-229,000	
N-Nap	10	7	2	1	+ 10,000	1-Nitro Naphthalene
G-53	5.143	9.75	1.938		-100,096	Polyester Polymer
EDM	10	14	4		-164,470	Ethylene Dimethacrylate
DPP	20	14	4		-115,900	Diphenyl Phthalate
PBENZ	13	10	2		- 57,700	Phenyl Benzoate
DPU	15	12	2	1	- 64,600	Diphenyl Urethane
AKARI	13	12	1	2	- 28,300	Diphenyl Urea
AKARII	14	14	1	2	- 34,100	Methyl Diphenyl Urea
DBP	16	22	4		-203,900	Dibutyl Phthalate
MC	15	16	1	2	- 14,180	Dimethyl Diphenyl Urea
Vinsol	16	19	3		-143,900	Trade Name
AKARIII	15	16	1	2	- 35,200	Ethyl Diphenyl Urea
EC	17	20	1	2	- 17,670	Diethyl Diphenyl Urea
Polystyrene	9	8			+ 17,422	
DOS	26	50	4		-344,210	Dioctyl Sebacate
Kraton	7	12			- 22,020	LOVA Binder Polymer
Polyethylene	2	4			- 12,700	
Arcwax	18	76	2	2	-181,000	Carbowax 400

Table II. Deterents Ranked by M9 T_{cv} at the Same Concentrations

	T_{cv} (K)	Impetus (J/gm)	T_{cv} (K)	Impetus (J/gm)
Base Grain M9	3837	1176		
Deterrent	7.5% Conc.		15% Conc.	
DNT	3664	1165	3440	1147
Camphor	3565	1117	3221	1046
x-Cellulose	3484	1121	3059	1042
N-Nap	3452	1138	2959	1055
G-53	3396	1076	2814	931
EDM	3375	1122	2820	1022
DPP	3343	1107	2723	983
PBENZ	3299	1197	2636	979
DPU	3285	1111	2619	978
AKARI	3284	1109	2612	972
AKARII	3270	1111	2590	973
DBP	3269	1199	2605	979
MC	3265	1114	2582	978
Vinsol	3256	1101	2567	963
AKARIII	3250	1108	2553	967
EC	3236	1113	2535	972
Polystyrene	3191	1088	2407	906
DOS	3110	1098	2334	935
Kraton	3022	1096	2220	916
Polyethylene	2961	1097	2150	897
Arcwax 200	2767	993	1640	717

A number of factors must be known to design a deterred propellant system with a minimum of trial and error[2]. These factors include chemical compatibility, chemical stability, deterrent penetration, ignitability, and burning rate modification. The most basic requirement is that the deterrent material be chemically compatible with the base grain ingredients. This is usually determined for short term purposes by such compatibility tests as Vacuum Stability, the Heat (methyl violet) test, thermogravametric analysis, Taliani, and differential scanning calorimetry. The long-term chemical compatibility is generally determined by accelerated aging studies where the ingredients are mixed together and stored at elevated temperatures for long time periods. Such factors as weight loss, color changes, changes in mechanical properties, and changes in chemical species concentrations are usually monitored. As a general rule the more reliable data are obtained at temperatures around 303-313 Kelvin over long time periods[5].

The next basic requirement is that the deterrent material be capable of penetrating the base grain matrix. Penetration is controlled by a large number of factors: the solubility of the deterrent in the coating solvent system; solvent levels in the base grain; nature of the base grain binder and plasticizer system; coating temperature; degree of agitation; deterrent melting point; deterrent molecular size; coating time; chemical interaction of functional groups on the deterrent and base grain ingredients; and deterrent concentration in the coating solution.

Most deterrents are applied at elevated temperatures in a solvent solution or suspension to propellant grains kept agitated by some means. The agitation prevents clumping of the grains during the impregnation, or as it is commonly called, the coating process, and encourages a uniform distribution of deterrent into all the surfaces of the grains, including the perforations. The result is illustrated in figure 1a.

In another experimental method the propellant strands are dipped into a super-saturated deterrent solution after extrusion but prior to cutting the strands into grains. This process allows the deterrent to penetrate only into the outer surface of the strand and not into the perforations or grain ends, and is illustrated in Figure 1b.

A similar coating of the extruded strands with a solution that does not penetrate into the surface produces a coating exterior to the strand surface. Materials applied in this manner are generally referred to as inhibitors and are illustrated in Figure 1b. Inhibitors prevent burning of the exterior wall of the strands or grains during some or all of the gun combustion cycle. As a rule, deterrent candidate materials that do not penetrate into the base grain, but form an inhibitor-like surface coating, cause clumping of the grains during storage and are unacceptable.

It is no trivial matter to determine the proper processing conditions and materials to produce an acceptable deterrent coating. The penetration is usually determined by chemical analysis of the bulk amount of deterrent impregnated into the grain, followed by closed bomb and ballistic firings[12]. Penetration depth can also be determined by such methods as optical analysis of thin sections of propellant grains where the deterrent

changes the optical density of the deterred region (sometimes hightened by staining techniques)[2]. Other methods can include chemical analysis of thin sections of the deterred regions to determine penetration depth and actual deterrent concentration in this layer[6].

Once the required penetration has been achieved, as determined by successful ballistic performance, the deterrent material should not migrate with time and temperature within the grain. Most deterrents are believed to penetrate the grain via a diffusion with binder interaction mechanism which results in a deterrent concentration profile as seen in Figure 4[6]. Note that the deterrent concentration is relatively constant throughout the deterred region with a very steep gradient at the deterrent penetration front. This produces a propellant grain which can easily be thought of as a two layered system consisting of the surface, low burning rate deterred layer surrounding the internal, higher burning rate, base grain regions. Experimental evidence with nitrocellulose (NC) binder systems suggests that the formation of, and the stability of, this type of deterrent concentration profile is the result of hydrogen bonding between the deterrent molecule and the binder[2,6,10]. This type of concentration profile may not hold true for polymeric deterrents which contain few chemical functional groups available for hydrogen bonding but rather depend on the overall size of the molecule to prevent migration.

Deterrent migration is generally evaluated by closed bomb determination of relative quickness (RQ) and relative force (RF). The freshly deterred propellant is tested and is then stored at some constant, elevated temperature (30-50°C) for at least three months. The RQ and RF are then determined again. Changes in RQ are primarily attributed to deterrent migration[12].

Deterrents tend to increase the ignition delay. In rapid firing weapons this can be a significant factor. In LCWS, with relatively slow rates of fire, this is not a major effect and should easily be resolved through a stronger ignition system. Ideally, the deterrent with the shortest ignition delay should be chosen when all other factors remain the same.

The base grain burning rate modification by the deterrent is the final and most important criterion. The deterrent may be chemically compatable, penetrate into the base grain, have good ignition, and not migrate, but all of these features are irrelevant if the deterrent does not reduce the burning rate of the base grain to produce the desired ballistic results. Only deterrents that can adequately modify the base grain burning rate in reasonable concentrations need be considered for compatibility, penetration, and migration evaluation with a given base grain formulation. The degree of this burning rate decrease effect would provide an initial screening criterion for deterrent/base grain selection and would greatly simplify and expedite the development process; it would also serve as input data in interior ballistic computer simulation codes to guide the development program.

Modern interior ballistic codes do a good job of modeling the performances of undeterred charges. The additional information required by these codes to model deterred systems consists of the thermodynamic data for the deterred region, the depth of deterrent penetration into the web, and the burning rate of the deterred region.

The required thermodynamic data can be easily calculated and consists of the impetus (force), Tcv, specific heats ratio of the combustion gases (gamma), the covolume, and for some codes, the average molecular weight of the combustion gases. The concentration of the deterrent in the deterred layer must be known to make these calculations. Since deterrent is confined to the outer layer, the actual deterrent concentration in the deterred layer is greater than the bulk concentration. While unique for each base grain, deterrent and weapon system application, the bulk concentrations of small arms deterrents typically range from one to ten percent of the total propellant weight with concentrations of the deterrent in the deterred region ranging approximately from ten to thirty percent[7].

Figures 5 and 6 show the changes in impetus and Tcv as a function of deterrent concentration in an M9 propellant base grain. As seen in these figures, the Tcv and impetus of the deterred layer in the 10 to 30 percent range is considerably different from the no-deterrent (base grain formulation) case. This supports our model of a deterred grain as, in the simplest case, consisting of two different propellants.

The burning rate of the deterred layer is the next piece of information required. For each base grain formulation, this will depend on the deterrent, its concentration, and the concentration profile in the deterred layer. With the change in base grain burning rate as a function deterrent concentration known, one could easily simulate existing deterred systems. Conversly, this data could be used to design deterred propulsion systems. The problem is that there is very little deterred layer burning rate data available. This situation must be rectified before effective modeling can occur.

Since burning rate reduction is the prime effect of deterrents, let us put aside the thermochemical effects for the moment. By considering a deterred grain as a two-propellant system, based on the concentration profile of Figure 4, interior ballistic codes could be used to determine the optimum differences in burning rates and the thickness of the deterred layer (depth of penetration) to provide the desired ballistic effect. From these results, a deterrent candidate could be selected that will produce the required reduction in burn rate as a function of concentration and the depth this concentration must penetrate to give the required results. This would not only allow efficient selection of deterrents, but also serve as a design guide in producing the required propellant.

DETERRED REGION BURNING RATE DATA

While there is a wide variety of available deterrent materials and an ever-increasing number of energetic base grain formulations, there

has been little direct experimental burning rate determination of compositions typical of deterred regions. However, there are at least two studies where the burning rate of a homogenous deterred system has been determined. In these studies various levels of deterrent were incorporated as part of the propellant composition during manufacture. This resulted in grains or strands with a uniform distribution of constituents throughout the grain or strand. Table III contains a summary of the compositions and reduced burning rate data of these studies.

In a study performed for BRL by Reiffler and Lowery of the Olin Corporation, two sets of propellants were produced to simulate single and double base compositions[8]. The double base compositions contained 8-10 percent nitroglycerine (NG). Both compositions used NC with approximately 13.1% nitrogen content. Duplicate ball propellant lots at various dibutyl phthalate (DBP) levels (a maximum of 16 percent DBP) were produced and the closed bomb burning rates determined. The initial effort was to determine the burning rate as a function of NG and DBP concentrations. Stiefel re-analyzed the data and correlated the burning rate as a function of the Tcv of each composition[7]. The correlation of the burning rate coefficient with a constant exponent of 0.8053 was determined to be

$$b = -0.8340 + 8.3956 \times 10^{-4} \text{ Tcv}$$

where

$$r = bP^n$$

and r = mm/sec burn rate, b = coefficient, P = MPa, n = 0.8053.

Stiefel's plot of the burning rate coefficient versus Tcv with the Riefler and Lowery data is given in Figure 7, and shows the best fitting straight line.

In a similar, unpublished effort, Moy determined the strand burner burning rate of a homogenous series of propellants with ethyl centralite (EC) deterrent[9]. The base grain composition consisted of NC (12.6 percent nitrogen) with 2 percent 2dinitro diphenyl amine stabilizer. Propellant formulations with EC concentrations of 0, 1, 5, 10 and 20 percent were produced and the strand burning rates determined. Our evaluation of these data at BRL determined the burning rate as a function of EC concentration to be

$$r_d = (0.96 - 0.12 \ln \text{ [EC]})r_0$$

where r_d = mm/sec burning rate of EC containing composition, r_0 = mm/sec burning rate of composition without EC, and [EC] = the EC concentration in percent.

The constant coefficient correlation of the Moy data between the exponent and Tcv, with a coefficient of correlation (R^2) of 0.995 is

$$n = 0.82945 + 5.5 \times 10^{-5} \text{ Tcv}$$

Table III   Summary Homogeneous Deterrent Burn Rate Data

A. RIEFLER AND LOWERY CLOSED BOMB BALL PROPELLANT LINEAR BURN RATE STUDY[8]

		LINEAR BURNING MODEL		BLAKE Tcv
% NC	% DBP	$b \times 10^{-4}$	n	(K)
SINGLE BASE NC (13.15 N)				
7.34	7.34	15.752	1.7388	2961
5.3	5.54	18.193	1.7665	2854
3.3	11.34	19.509	1.7540	2245
0.23	16.26	52.253	0.7206	1964
DOUBLE BASE NC (13.15 N)				
10.99	0.99	10.144	0.8531	3155
4.75	3.95	3.137	0.9301	2845
4.10	13.90	11.932	0.7424	2159
3.12	16.65	09.509	0.7489	2034

B. A. WW STRAND BURNER DETERRENT STUDY[9] (69-310 MPa DATA)

PROPELLANT	BASE FORMULA		DETERRENT
	89.9% NC (12.6% N)		100% ETHYL CENTRALITE
	0.2% 2NDPA		

STRAND	% EC	$b \times 10^{-4}$	n	BLAKE Tcv (K)
3.0	1.986	1.027	3086
1.0	1.62	2.3648	2999
7.0	1.000	1.9993	2647
10.0	1.90	0.980	2231
20.0	0.70	0.315	1879

where

$$r = bP^n$$

and, $r = mm/sec$, $b = 0.003$ and $P = psi$.

The constant exponent correlation between coefficient and Tcv with an R^2 of 0.995 is

$$b = (4 \times 10^{-5} + 6.056 \times 10^{-8} \text{ Tcv}) 25.4$$

where

$$r = bP^n$$

and

$$r = mm/sec, \quad n = 0.9776 \text{ and } P = psi$$

A plot of the correlation of both constant exponent and constant coefficient with composition Tcv is seen in Figure 8. The best fitting straight lines are shown.

We attempted to correlate the burning rate effects of both these studies into a single expression. Numerous combinations of Tcv, average gas molecular weight, covolume, and adiabatic pressure with the reported burning rates from a first to a third degree multiviarant linear regression analysis failed to give a useful correlation. Reasons for this lack of correlation could include the differences in burning rate determination methods and the differences in nitrogen content of the NC (13.1 and 12.6 percent). However, in both studies the burning rates are strong linear function of the composition Tcv, which ranged from 1900 to 3200 Kelvin in both efforts. More experimental data are needed to develope a unified expression for predicting deterred region burning rates in any base grain over a wide Tcv range.

DESIGN OF DETERRED SYSTEM

Deas and Trafton used the Riefler and Lowery burning rate study formula (based on ingredient concentrations) to determine the theoretical optimum performance obtainable with a hypothetical high-energy double-base propellant, roughly equivalent to M9 propellant, with DBP deterrent[3]. The design test bed was the M68, 105mm tank gun firing KE ammunition. Double-base propellant was chosen, as it is an energetic propellant that is readily producable. The goal was to predict performance gains available from a propellant (with a higher energy than the standard M30) both with and without a deterred layer.

For their analysis, the bulk concentration was set at 2, 4, and 6 percent DBP. At each bulk concentration the deterred surface layer concentration (SLC) was varied at 7, 9, 13, and 17 percent DBP. The depth of penetration was determined by the SLC. Thus the higher the SLC, the less the deterrent could penetrate. The web at each charge weight and SLC was varied to give the same peak pressure. The results are seen in Figure 9.

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This theoretical analysis determined the optimum conditions to be a 2-4 percent bulk concentration with a 7-9 percent SLC. This deterrent combined with a 19-perforated base grain gave a predicted 10-percent velocity improvement over the standard M30 propellant in the 105mm design system. Three percent of this gain was due to the deterrent.

DBP was chosen as the deterrent for this theoretical study because of the availability of burning rate data but it is not a realistic choice. DBP tends to migrate in propellants containing more than 20 percent NG^2; and thus a problem remains of selecting a suitable replacement for DBP in order to test these predictions experimentally.

We used the strong dependency of the deterred layer burning rate on Tcv to develop a useful design tool for selecting a DBP replacement. We assumed that any chemical effects of deterrent candidates on the base grain burning rate are minimal and accounted for in the calculation of Tcv. As M9 is a double base propellant, Stiefel's correlation was used as a yardstick to compare the relative burning rate effects of candidates to that of DBP. Deterrents that have Tcv's similar to DBP at the same concentration should modify the base grain burning rate almost the same as DBP. Thus viable, direct DBP replacements could be selected in a rational manner. Then other factors such as penetration behavior and migration effects could be used for evaluation and final selection.

One note of caution is seen in Figure 6. Note that all the curves are more or less linear down to about 2200 K. Below this temperature we recognize that our linear correlation model will be invalid and care should be exercised in making comparisons.

Table II lists a number of candidates to replace DPB which are ranked by TCV at a 7.5 percent concentration in M9. Based on the Stiefel correlation, a +70 K Tcv variation around the Tcv of DBP at 7.5 percent gives a burning rate variation of about ± 5 percent. This provides a reasonable rule of thumb to select a direct DBP replacement. There are a number of materials in the table that fall within the range.

The candidates in this range are all close to the same molecular weight but should have different penetration and migration effects. Diphenyl phthalate (DPP), a slightly higher molecular weight analog of DBP, has been used to replace DBP in highly plasticized binders (>20 percent NC). Due to the larger phenyl group, DPP could be expected to penetrate less than DBP, but also to migrate less than DBP. Broadman and Devine also suggest this type of behavior by DPP is due to the greater electron contributing effect of the phenyl group which makes the carbonyl oxygen of the phthalate group more electronegative, thus forming stronger hydrogen bonds with NC than $DBP^{10,11}$. The other materials in the group around DBP should demonstrate similar subtle penetration and migration differences.

Deterrents with higher Tcv's than DBP will require higher concentrations to achieve the same burning rate modification. Camphor at the 15 percent concentration has about the same Tcv as DBP at 7.5 percent. Thus, for the same burn rate change, camphor would need about twice the concentration as DBP at the same penetration. The opposite trend should be true for

such materials as Arcwax, which is about 15 percent cooler than DBP at the 7.5 percent concentration.

Once the deterrents are ranked by T_{cv}, the next factors to consider are the gross penetration and migration effects. Due to the high plastisizer content of M9, molecules, molecules similar in size to DBP may migrate. One solution is to use much larger or even polymeric molecules. Arcwax is such a large molecule, but due to its size, there may be a problem in achieving the same penetration depth at the lower concentration necessary to give the same burning rate effect as DBP. Due to size alone, Arcwax will form a narrow, high SLC with very low burning rates. G54-Paraplex (Hurkote) is a polyester polymer and should show similar size effects as Arcwax but, with its higher T_{cv} than DBP at 7.5 percent, the burning rate modification of G54 will be less than Arcwax at the same SLC. Thus G54, while still tending to form a high SLC, is favored over Arcwax. Another advantage of G54 is that, along with its high molecular weight, it has sites available for hydrogen bonding. Both of these are features which prevent migration.

Of direct interest to producing a propellant with any deterrent is the sensitivity of ballistic performance to SLC variation, i.e., depth of penetration. The general trend seen in Figure 9 is, that the lower the bulk concentration, the less sensitive the performance is to depth of penetration, i.e., the SLC curves are closer together. This lowered sensitivity provides an important design feature. Using low bulk concentrations will allow greater flexibility in the processing conditions which control depth of penetration. This flexibility will help insure lot-to-lot performance uniformity, a major problem in deterred propellant manufacture.

Should it become a problem, the deeper penetration required by the four percent bulk concentration could be achieved by harsher deterring conditions such as stronger solvent systems, higher temperatures and more residual solvent in the base grain. These conditions in a double base system such as M9 tend to leach out the NG. This reduces the overall energy of the finished propellant and the NG contamination of the coating solvent system complicates processing. The two percent bulk concentration plot shows far less sensitivity to depth of penetration. This deterrent level should make production easier and still provide significant performance gains. While this analysis indicates trends, experimental penetration and migration data with M9 is needed before a rational choice can be made.

EXPERIMENTAL EFFORTS

A development program is underway at Radford Army Ammunition Plant (RAAP) to evaluate those concepts for demonstration in the 105-mm tank gun. The initial stage of this effort consists of deterring M9 grains in the laboratory under identical processing conditions (typical of large scale production) at two or more coating levels. The initial selection of deterrent candidates will come from Table II. The change in base grain RF and ?Q will be determined as well as the bulk and deterred layer concentrations. Determination of the deterred layer burning rate will be attempted via closed bomb analysis.

Based on the penetration and burning rate data, several large scale lots of ballistic and homogeneous deterred lots will be produced. The ballistic lots will be deterred and, after analysis at RAAP, test fired at BRL. The homogeneous lots will be produced for closed bomb burning rate analysis at BRL. This effort will not only develop a high energy, deterred propellant for the M68 tank gun, but also validate the design concepts presented.

The initial laboratory results from RAAP indicated that the ethyl alcohol-water solvent system typically used at RAAP to soften small arms grains prior to adding the deterrent was having two main effects. The first was that the M9 grains were being softened too much, causing clumping and grain deformation upon drying. An explanation is that the high NG content in M9 may be causing the grains to be too soluable in the normal softening solution. Another factor may be that propellant grains for the 105-mm gun are much larger than a typical small arms grain. This means that the LCWS grains have a much smaller surface area per unit mass than small arms grains. Thus it takes longer for the same amount of alcohol to penetrate into the smaller surface area of the same mass of LCWS grains. This results in a higher alcohol concentration for a longer time period at the LCWS surface. This coupled with the higher soluability of M9 in the ethyl alcohol softening agent may be producing the observed results. The concentration of the alcohol is being reduced to solve this problem.

The second effect of the softening solvent found in the laboratory study was that, even under the mild, small arms-type coating conditions, the NG was being leached out. Closed bomb analysis of samples run through the processing conditions without a deterrent showed a significant reduction in RQ. This effect is being analyzed further. Should these initial results prove valid, this may provide a useful method for generating an exterior, low burning rate region in propellants using high concentrations of energetic plasticizers.

The next step was to use the laboratory results to coat 22.5 kilogram (50 pounds) batchs of M9 propellant in the production coating equipment with C 54 and methyl centralite. The first attempts were at a coating temperature of 67°C. This resulted in excessive softening of the grains with both deterrents. From this effort it was discovered that about 90 percent of the deterrent added in the coating solution was being taken up by the grains.

From these results it was decided to reduce the coating temperature. Subsequent coatings were made at 55 and 45°C with the same solutions and deterrent concentrations as attempted at 67°C. The coatings at both temperatures appeared acceptable. The analysis of these efforts are still in progress and further data was unavailable at the time this report was written.

FUTURE EFFORTS

In order to expand the deterrent technology data base, several future efforts are planned. While M9 is high in energy and easily produced, its high flame temperature will cause barrel erosion and possibly flash problems. Some of these effects will be ameliorated by the deterrent. Future efforts will include developing deterrents for

Table 1. Energetic Deterrents

DETERRENT	EMPIRICAL FORMULA				ΔH_f Cal/mole	NAME/DESCRIPTION
	C	H	O	N		
PROPYL NENA	5	11	5	3	- 42,603	N-Alkyl Analogs of
BUTYL NENA	6	13	5	3	- 46,702	Nitrato ethyl
PENTYL NENA	7	13	5	3	49,905	nitramine (NENA)
HEXYL NENA	8	17	5	3	- 52,905	
HEPTYL NENA	9	19	5	3	56,234	
BTTN	3	7	2	4	+252,700	3,3 Bis nitridomethyl oxetane
DNBN	5	5	2	3	+ 17,600	Dinitraza Butyl Nitril
GAP	3	6	2	3	+ 53,700	Glycidyl Azide Polymer

Table 2. Energetic Deterrents Ranked by Tcv in M9 Propellant

DETERRENT	15% Conc		15% Conc	
	Tcv (K)	Impetus (J/gm)	Tcv (K)	Impetus (J/gm)
GAP	3715	1192	3564	1205
BTTN	3707	1191	3545	1194
PROPYL NENA	3686	1184	3549	1187
BUTYL NENA	3464	1182	3455	1175
DNBN	3604	1165	3440	1142
GAP	3615	1164	3430	1173
PENTYL NENA	3627	1179	3371	1169
HEXYL NENA	3592	1177	3291	1159
HEPTYL NENA	3545	1174	3230	1153

high energy, lower flame temperatures propellants based on solid filled,
nitramine systems. Similar efforts to the present M9 program are planned
using this type of propellant. This will also include determining
deterred homogeneous burning rates of various deterrents with these
nitramine base grain formulations.

Traditional deterrents lower both the impetus and Tcv of the base
grain. This reduction in energy offsets the gain of burning rate control
by requiring an increased charge loading to replace the energy lost due
to the deterrent. What if the impetus could be maintained while the
flame temperature and burning rate is reduced? There are several low
Tcv, high energy materials being developed to replace the high Tcv
plasticizers such as NG and to replace NC as the only choice for a high
energy propellant binder. Table IV is a listing of some of these materials
and Table V is a comparative ranking of the Tcv at the same concentration
in M9. A useful comparison can be made with DNT, the most energetic
deterrent in common US propellants, and which can be seen to have a high
Tcv (Table II). By assuming that the burning rate is a function of Tcv,
the correlation of burning rate with flame temperature determined by
Stiefel can be used to predict the change in burning rate produced by
the materials.

Figure 10 is a comparison of the predicted change in M9 burning
rate at a 20-percent concentration of a variety of standard and energetic
deterrent materials as compared to the change the same concentration of
DNT is predicted to give. With DNT as our yardstick, GAP, NBN and
Propyl NENA do not lower the M9 burning rate as much as DNT. Indeed GAP
and NBN are being developed to provide increased burning rates. The
alkyl NENA's above Butyl NENA as well as the BAMO polymer show promise.

Figure 11 compares the impetus of these materials at a 20-percent
concentration to the M9 base grain impetus. Note that a 20-percent
concentratin of Heptyl NENA has about the same impetus as the same
concentration of DNT, while providing a greater burning rate reduction
due to the lower Tcv than DNT as seen in Figure 10.

While admittedly a crude analysis, the data do suggest that the
development of energetic, low flame temperature deterrents is possible.
These materials will be included in the laboratory scale coating efforts
at RAAP in FY82.

CONCLUSIONS

Designing and developing deterred propellant systems for LCWS in a
rational manner requireds knowing the effect of a deterrent on the base
grain formulation's burning rate. From an analysis of the limited
deterred layer burning rate data available, a method for predicting this
burning rate effect has been developed based on the strong linear correlation
of burning rate with the adaibatic, isochoric flame temperature of the
deterred region down to about 2000 K. This theoretical correlation
based on thermochemistry does not predict exact burn rate effect in

every base grain, but does provide relative comparisions. Using this correlation several promising deterrent candidates for an M9 double base propellant have been selected for evaluation in the 105-mm tank gun. A significant achievement of this methodology is the selection of five deterrent candidates which exhibit a decrease in burning rate without the energy loss associated with traditional deterrents. This analysis is being used to guide a deterrent development program now ongoing at RAAP.

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BASE GRAIN
PERFORATION

STANDARD
DETERRENT
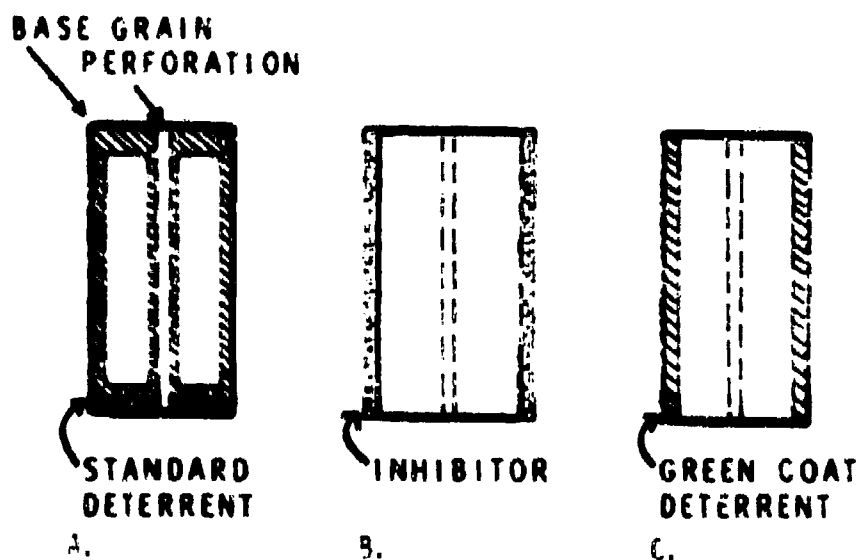A.

INHIBITOR
B.

GREEN COAT
DETERRENT
C.

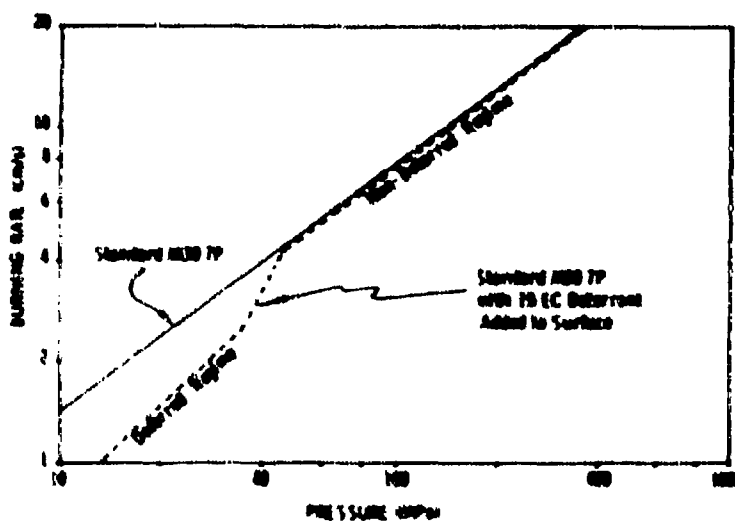Figure 1. Examples of Deterrent- and Inhibitor-Treated Propellants

Figure 2. Burning Rate of M30 7P Propellant, Standard and
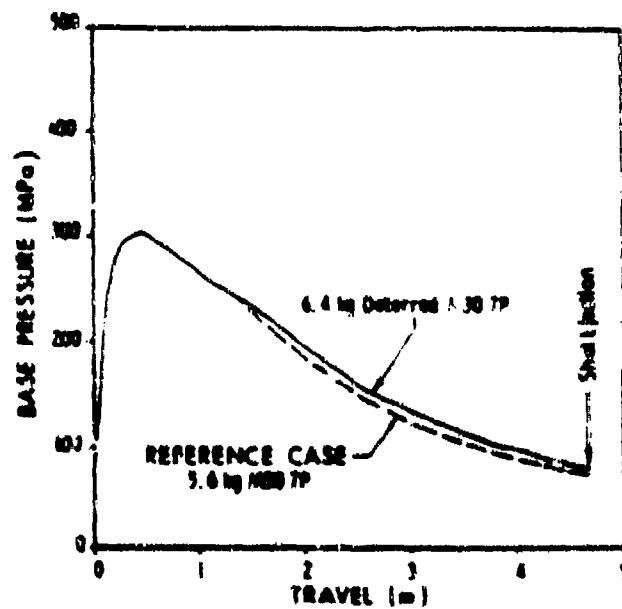Deterred (Reference 3)

Figure 3. Base Pressure vs Travel with Standard and Deterred M30
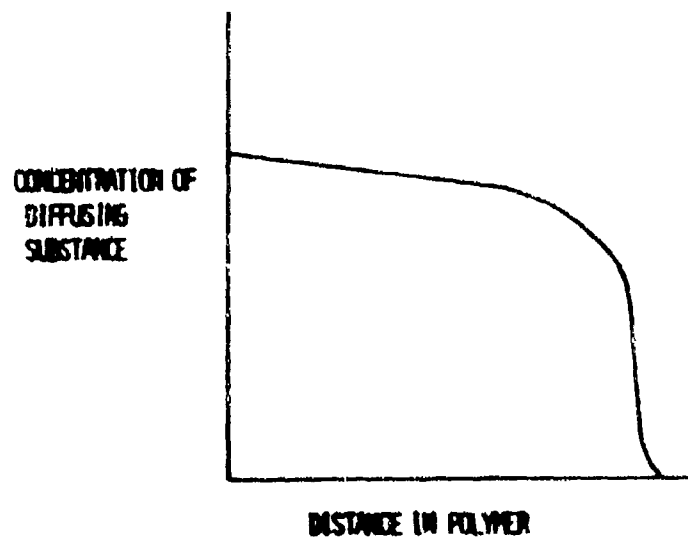7P Propelling Charges (Reference 3)

Figure 4. Deterrent Concentration Profile Produced by a Diffusion
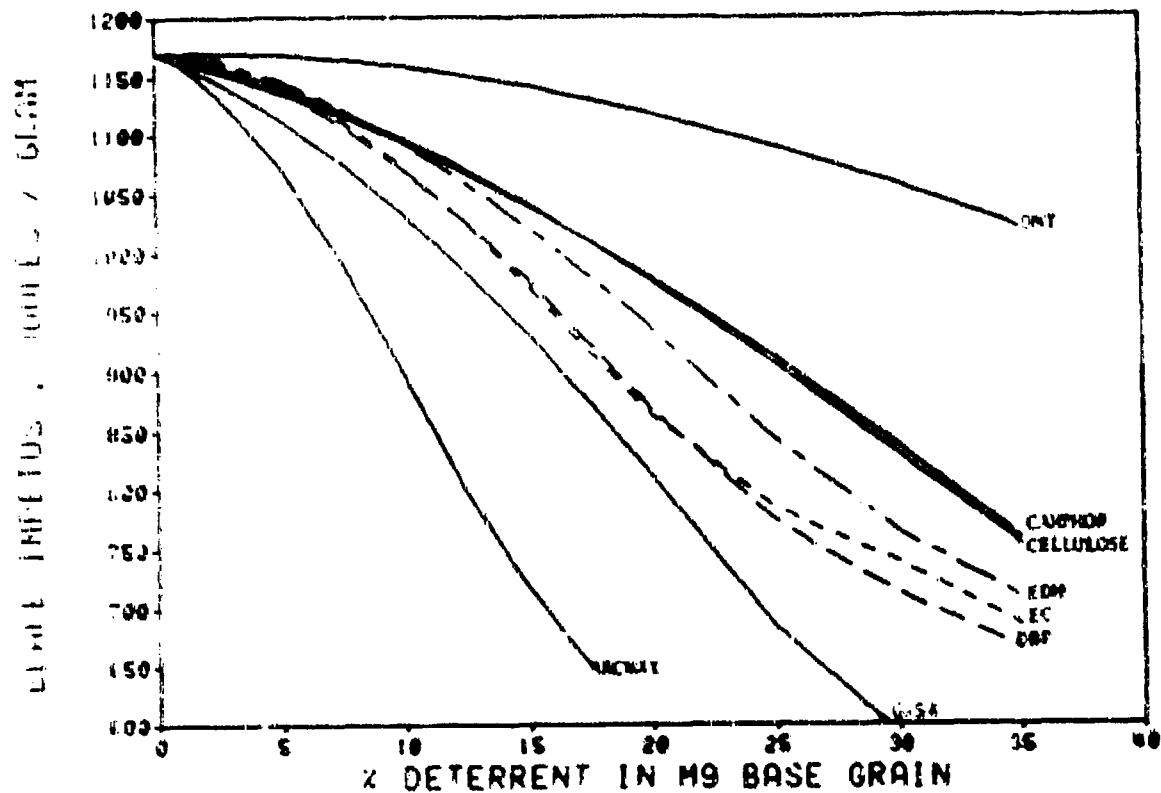with Interaction Mechanism (Reference 6)

Figure 5. Plot of Change in Impetus of Selected Deterrents from Table II in an M9 Base Grain
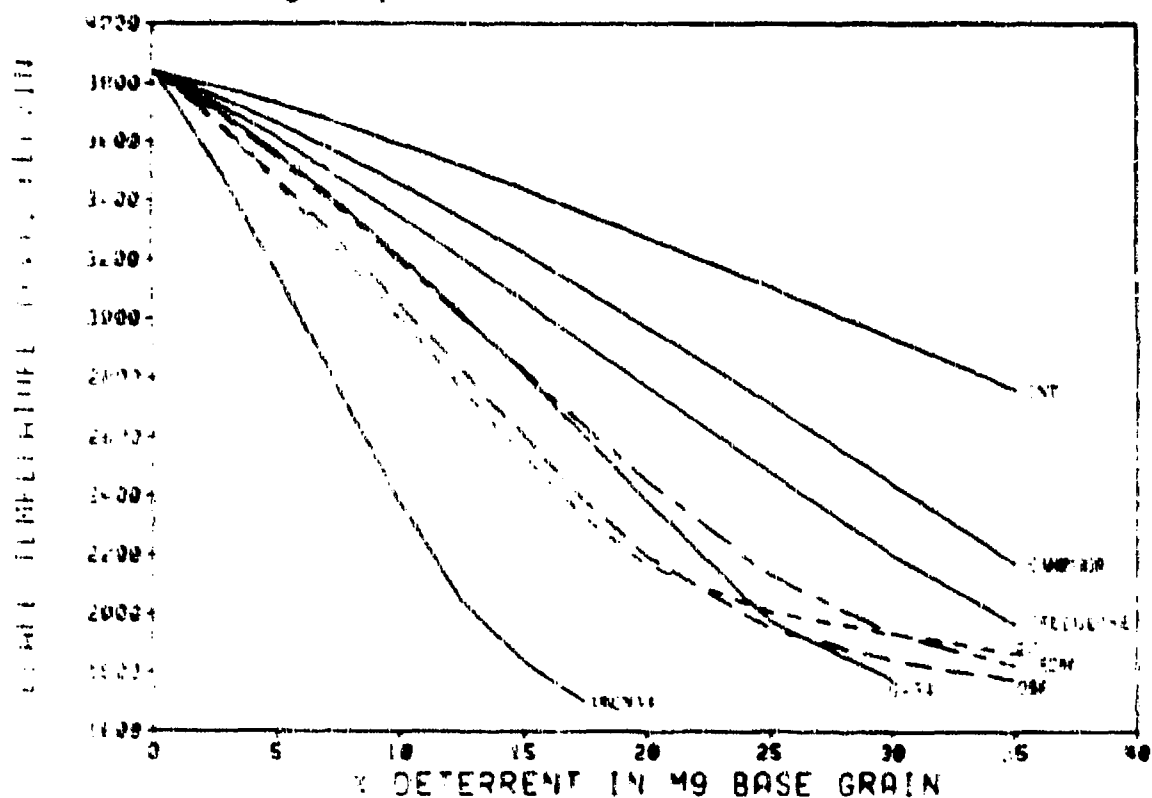
Figure 6. Plot of Change in Isochoric Adiabatic Flame Temperature of Selected Deterrents from Table II in an M9 Base Grain
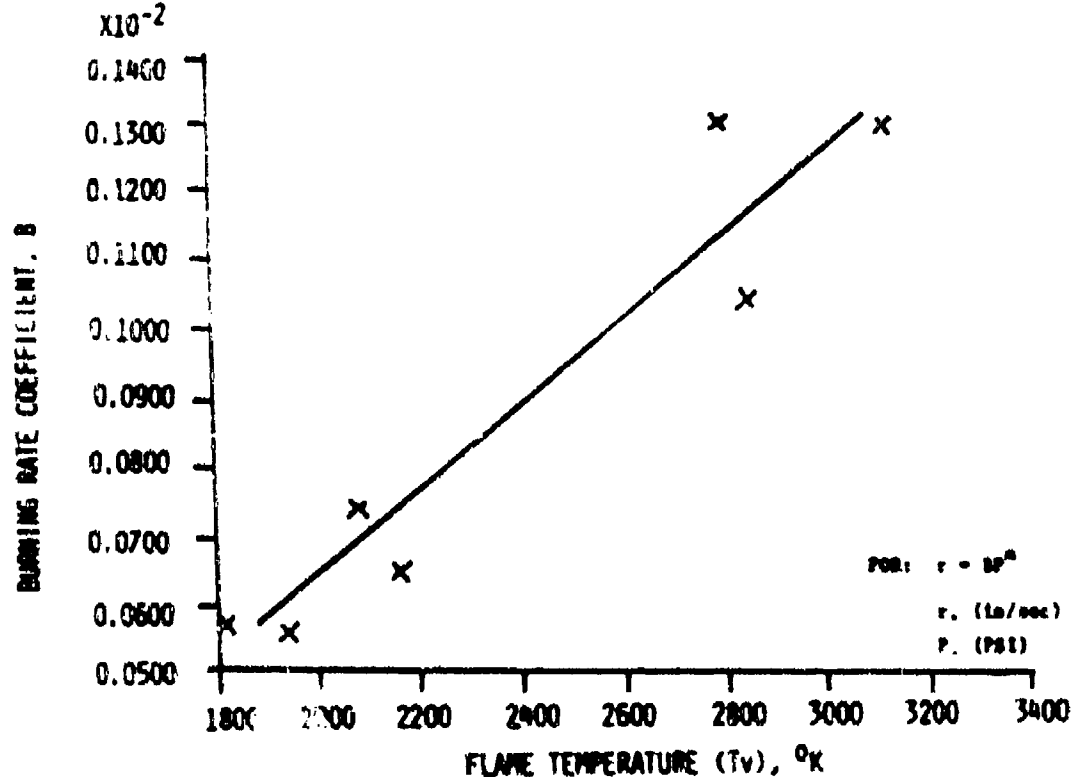
Figure 7. Correlation of Riefler and Lowery Burning Rate Data, Ref. 13, with Flame Temperature by Stiefel, Ref.
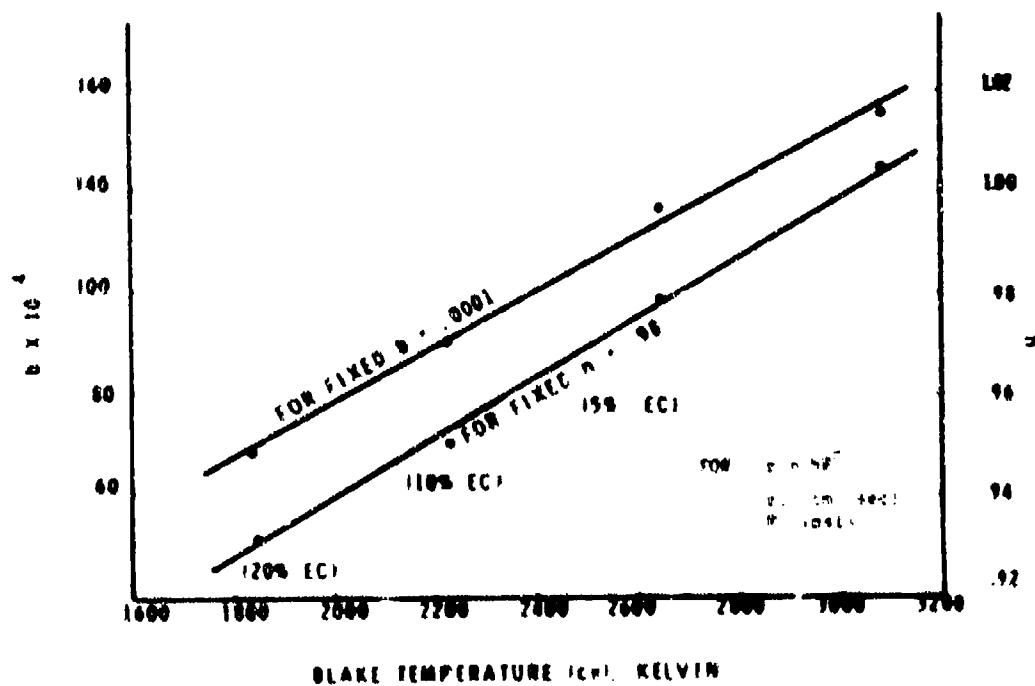
Figure 8. Correlation of Max Burning Rate Data, Ref 8, with Flame Temperature with Both a Constant Exponent, n, and Coefficient b

2% DBP Bulk
Concentration
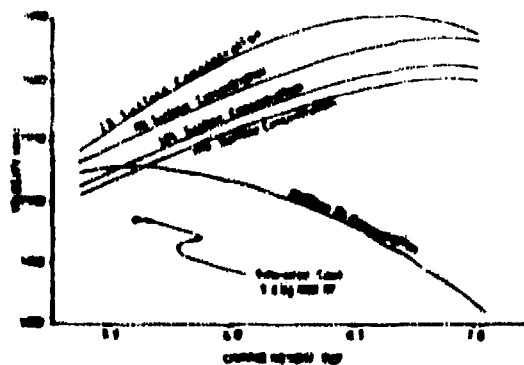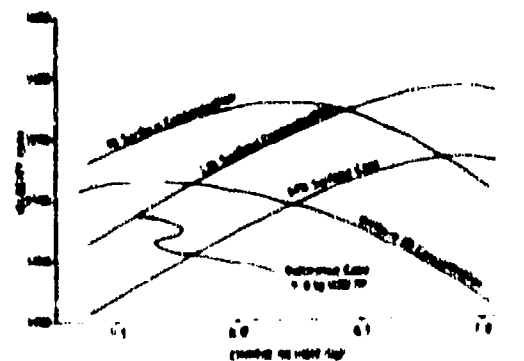
4% DBP Bulk
Concentration
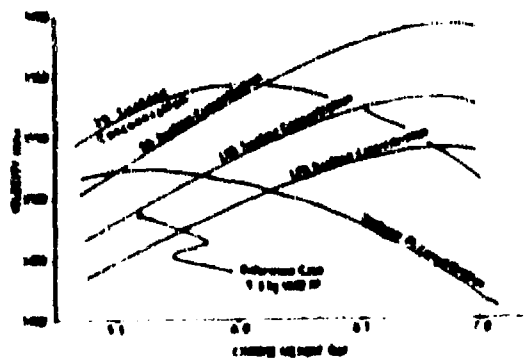
6% DBP Bulk
Concentration

Figure 9.   Predicted Velocity of Deterred High-Energy 19-Perforation
            Propellant with Varying Deterrent Levels (P_{max} = 415 MPa)
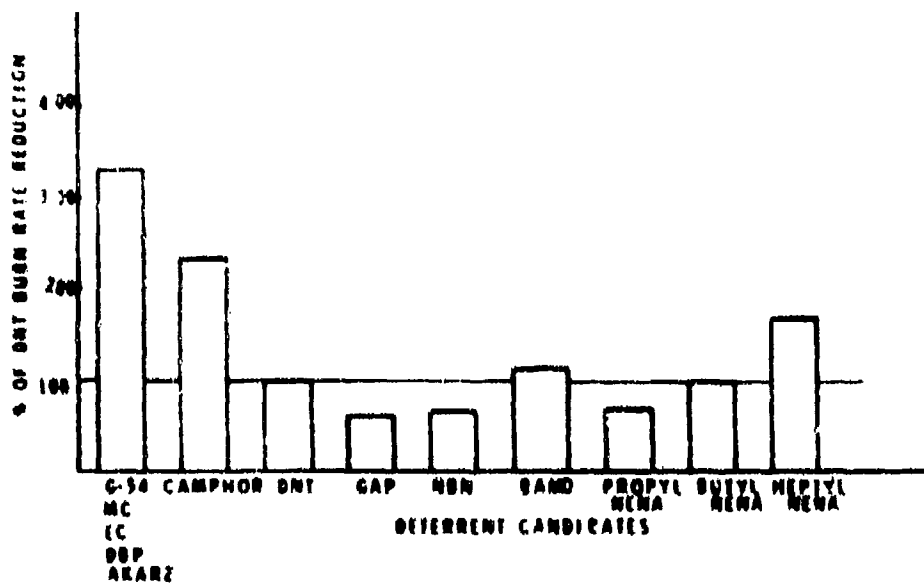   (Reference 3)

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Figure 10. Predicted Burn Rate Reduction of M9 with Various Deterrents
(20% Deterrent Concentration)
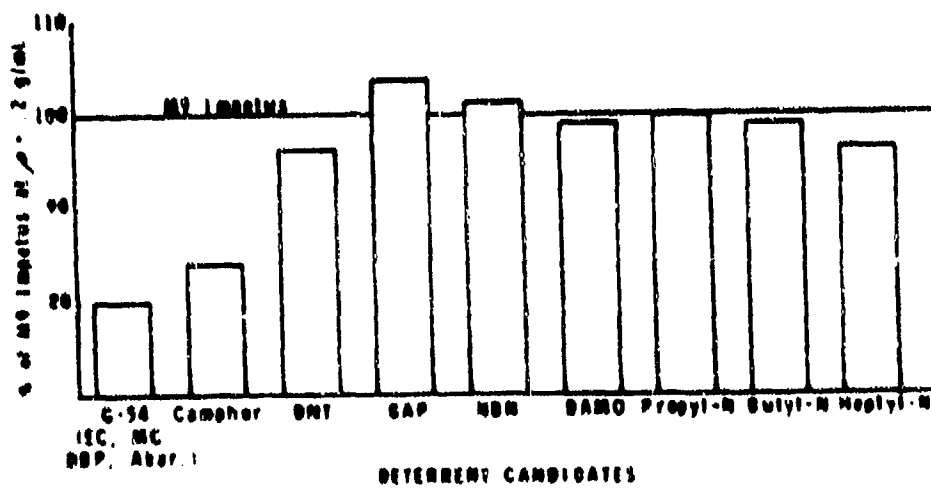

Figure 11. Impetus of M9 with various Deterrents at a 20% Concentration